(12) UK Patent Application (19) GB (11) 2 274 284 (13) A

(21) Application No 9326099.0

(22) Date of Filing 21.12.1993

(30) Priority Data
(31) MI92A2938 (32) 23.12.1992 (33) IT

(71) Applicant(s)
Snamprogetti S.p.A.

(Incorporated in Italy)

Corso Venezia 16, Milan, Italy

(72) Inventor(s)
Domenico Sanfilippo
Luca Basini

(74) Agent and/or Address for Service
Haseltine Lake & Co
Hazlitt House, 28 Southampton Buildings,
Chancery Lane, LONDON, WC2A 1AT,
United Kingdom

(51) INT CL^5
C01B 3/38

(52) UK CL (Edition M)
C5E EAS E101 E111 E122 E124 E125

(56) Documents Cited
EP 0576096 A2	EP 0548679 A1	EP 0330751 A2
EP 0303438 A2	WO 93/01130 A1	US 4897253 A
US 4844837 A	US 4620940 A	

(58) Field of Search
UK CL (Edition M) **C5E EAR EAS**
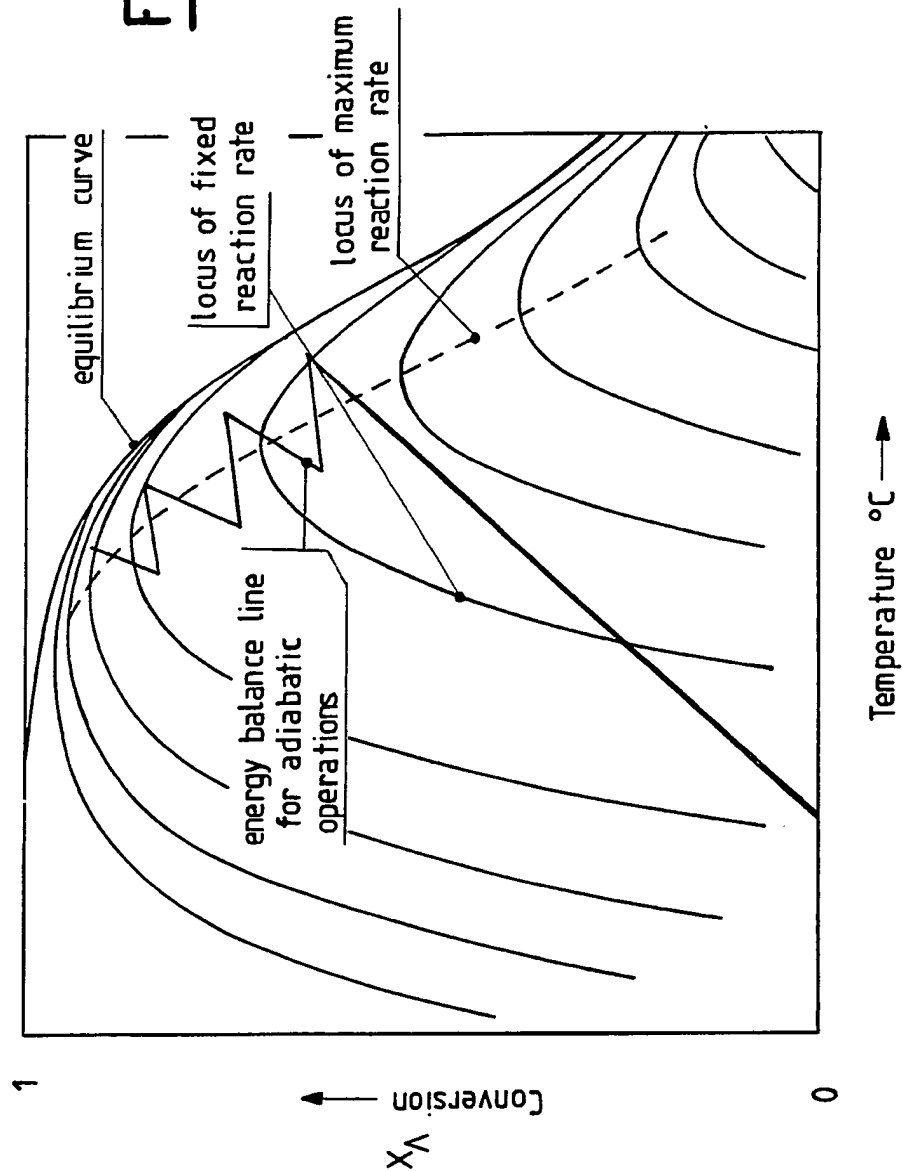INT CL^5 **C01B 3/34 3/36 3/38 3/40**
ONLINE DATABASE: WPI

(54) **Catalytic process for producing synthesis gas**

(57) Catalytic process for producing synthesis gas by starting from methane, oxygen and optionally carbon dioxide and water, in which a noble metal catalyst supported on a solid carrier is used, which catalyst is arranged as a cascade of a plurality of catalytic beds, and the process is carried out under adiabatic conditions:
-- by feeding the gas reactant stream upstream of the first catalytic bed and removing heat by heat exchange between the catalytic beds arranged in cascade, or
-- by introducing the gas reactant stream partially upstream from the first catalytic bed and partially, as a cold stream, between the catalytic beds arranged in cascade, with the proviso that methane is at least partially fed to the first catalytic bed and oxygen is subdivided between all of the catalytic beds.
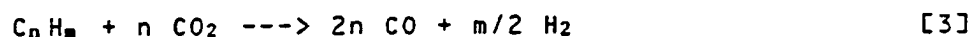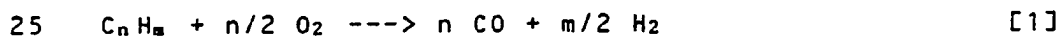
GB 2 274 284 A

Fig.1

equilibrium curve

locus of fixed reaction rate

locus of maximum reaction rate

energy balance line for adiabatic operations

Conversion ⟵

y_x

1

0

Temperature °C ⟶

"CATALYTIC PROCESS FOR PRODUCING SYNTHESIS GAS"

The present invention relates to the production of synthesis gas ("syngas") by starting from methane, oxygen and, possibily, carbon dioxide and water, which process is carried out over a plurality of catalytic beds arranged in cascade and feeding the feedstock to the process as a plurality of subdivided streams fed upstream from each catalytic bed.

The synthesis gas, also referred to as "syngas" is prevailingly constituted by a gas mixture of CO and H_2. Producing the syngas mixture is presently the key passage in the technology of production of fuels for motor vehicles by means of Fischer-Tropsch synthesis, in the technology of production of methanol and higher alcohols, and in ammonia synthesis. The investment costs and energy consumptions for operating the production units for syngas are estimated to be approximately 60% of total costs of the above listed processes.

Syngas is presently produced by means of steam reforming or auto thermal reforming or processes of partial, non-catalytic, oxidation of hydrocarbons. The reactions which constitute the base of these conversions are the following:

$$C_n H_m + n/2 \ O_2 \longrightarrow n \ CO + m/2 \ H_2 \qquad [1]$$

$$C_n H_m + n \ H_2O \longrightarrow n \ CO + (m + n/2) \ H_2 \qquad [2]$$

$$C_n H_m + n \ CO_2 \longrightarrow 2n \ CO + m/2 \ H_2 \qquad [3]$$

$$C_n H_m \longrightarrow C_n + m/2 \ H_2 \qquad [4]$$

$$2CO \longrightarrow C + CO_2 \qquad [5]$$

$$CO + H_2O \longrightarrow H_2 + CO_2 \qquad [6]$$

In greater detail, the steam reforming processes catalytically convert hydrocarbons/steam mixtures (H_2O:C=2.5 - 3.5), yielding CO/H_2 mixtures with an H_2/CO ratio which typically is of round 3. The

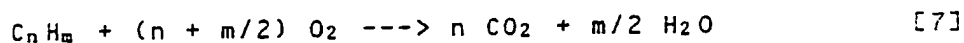5 chemical reactions involved in the process are [2], [4-5] and [6].

The H_2O/C ratio in the reactant mixture is both determined by the temperature and pressure conditions under which the reactions are carried out, and by the

10 need of inhibiting the coal formation reactions [4-5]. The commonly used catalysts in these processes are based on Ni supported on Al, Mg, Si oxides. These carriers display high characteristics of heat stability and mechanical strength. The reactions are

15 carried out inside tubular reactors installed inside a combustion chamber. The pressures inside the tubes are typically comprised within the range of from 1 to 5 MPa, and the gas temperature at tube outlets typically is of round 850°C (reference is made, for instance, to

20 "Catalysis Science and Technology"; Vol. 5 (1984), chapter 1, J.R. Rostrup-Nielsen).

The non-catalytic partial oxidation processes are less widely used and are employed in order to convert mixtures of oxygen, hydrocarbons, steam and water into

25 syngas with H_2/CO ratios of typically round 2. The chemistry of the process can be represented by the equations [1], [4]-[6]. The facilities installed heretofore by Texaco and Shell (see Hydrocarbon Processing; April 1990, page 99) use adiabatic

30 reactors inside which the reactions are initiated at

reactors inlet by means of a burner in which total hydrocarbon combustion reactions [7] take place. These reactions produce large heat, steam and CO_2 amounts. Heat causes reactions of cracking of unburnt

5   hydrocarbons and favours the steam [2] and CO_2 [3] reforming reactions.

The operating temperatures are typically comprised within the range of from 1250 to 1500°C, and the pressure is allowed to range from 3 to 12 MPa.

10   The processes of autothermal reforming are carried out inside adiabatic reactors to which mixtures of hydrocarbons, oxygen and steam are fed. In a first reaction zone, the reactions are initiated of total combustion of hydrocarbons, represented by the

15   equation:

$$C_n H_m + (n + m/2) O_2 \longrightarrow n CO_2 + m/2 H_2O \qquad [7]$$

In a second zone inside a catalytic bed, the steam [2] and CO_2 [3] reforming reactions take place. In the catalytic bed, nickel-based catalysts are used, the characteristics of which are analogous to those as

20   described above for steam reforming processes. In the autothermal reforming, mixtures of H_2/CO having values ranging from those of steam reforming processes to those of non-catalytic partial oxidation, are obtained.

25   ―――――――――――――――――――――――――― The temperature of the gas streams at reactor outlets is typically comprised within the range of from 950 to 1000°C, but the temperature of the zone in which the burner is installed is considerably higher. The pressure inside

30   the reactors is comprised within the range of from 2

to 4 MPa.

One from the main drawbacks which limit the possibilities of technological innovation in the definition of new catalytic reactors and new processes

5 routes for syngas production and use is determined by the coal formation reactions [4]-[5]. Coal formation is not tolerated in the catalytic processes for syngas production and is prevented from occurring by using reactants mixtures containing steam and/or oxygen.

10 According to the syngas production processes and the operating conditions, therefore, restraints exist as to the composition of the reactant mixture and, in particular, as to its steam and/or oxygen contents; such restraints are generally expressed in terms of

15 H_2O/C and O_2/C ratios.

Extending the threshold values of composition of the reactant mixture, would make it possible innovative solutions to be designed for syngas production processes, because one might state that the

20 characteristics of the reactors and of the process schemes in syngas production facilities are the result of complex interactions between the chemical properties of the catalysts and mechanical constraints to the characteristics of the materials used in the

25 reactors.

In Italian patent application No. 19,162 A/90, filed on January 26th, 1990, to the same Applicant's name, disclosed is a process for syngas production by starting from carbon dioxide and light hydrocarbons,

30 in particular methane, over a supported catalyst based

on a metal from platinum group. Furthermore, in Italian patent application No. 21,326 A/90, filed on August 29th, 1990, to same Applicant's name, disclosed is a process for syngas production by means of a first

5   step, of non-catalytic combustion of hydrocarbons with oxygen, followed by a second step, of reforming, in which the oxidation products from the first step are brought into contact with a further amount of hydrocarbons, in the presence of a supported catalyst

10   of a metal from platinum group.

The present Applicant found now, according to the present invention, that the use of noble metal catalysts considerably reduces the width of the regions inside which the coal formation reaction takes

15   place and therefore makes it possible reaction mixtures with low H_2O/C (e.g., lower than 0.5) and O_2/C ratios (e.g., lower than 0.5) to be used without that the coal formation reaction are initiated.

Such a finding makes it possible said catalysts

20   to be used in a process for syngas production in a reaction system consisting of a plurality of adiabatic catalytic beds arranged in cascade, in which a differentiated feed of the reactant mixture is preferably provided, and in which the composition of

25   said mixture at the inlet to said catalytic beds may even have values of H_2O/C and O_2/C ratios, which are lower than 0.5 and 0.5, respectively. Furthermore, a catalytic process which displays such characteristics makes it possible syngas mixtures to be obtained

30   withour requiring that at its inlet a burner is

installed, because the combustion reactions are catalytically initiated at low temperatures.

More particularly, the process for syngas production, carried out on a plurality of adiabatic catalytic beds in cascade, according to the present invention, enables the following advantageous effects to be accomplished:

-- reduction of temperature gradients and also of the highest temperature values inside said catalytic beds, with consequent lower thermal stresses being applied to the materials; in that way, traditional building materials can be used, with consequent savings in investment costs;

-- possibility of directly obtaining, at the outlet from the catalytic partial oxidation reactor, syngas with H_2/CO ratios comprised within the range of from 0.9 to 3, without that the adjustment of the value of such a ratio requires that a further reactor for water gas shift (WGS) reactions [6] is used;

-- possibility of avoiding using a burner at reactor inlet, with consequent saving in reactor investment costs;

-- improvement of heat efficiency of syngas production process, both as compared to the commercial processes of non-catalyzed partial oxidation processes, and as compared to autothermal reforming processes; such an improvement is made possible because the configuration of the reactor makes it possible the heat recovery rates to be optimized,

by preventing the unnecessary, extremely high
temperatures which occur inside the interior of the
reactors (in particular at inlet regions) used in
the exisiting processes;

5   -- possibility of kinetically controlling the coal
generation reactions and, therefore, of reducing
the values of H_2O/C (steam mols/carbon mols) and
O_2/C (oxygen mols/carbon mols) ratios in the
reactant mixture;

10   -- possibility of optimizing the process conditions,
with in each layer the conditions of maximal
reaction speed being reached, with the catalyst
amount being consequently decreased (decreasing the
catalyst amount is a determinative factor when

15   noble metal-based catalytic system are used).

In accordance therewith, the present invention
relates to a catalytic process for preparing synthesis
gas by starting from methane, oxygen and, possibily,
carbon dioxide and water, characterized in that:

20   -- the catalyst used is a noble metal catalyst
supported on a solid carrier, arranged as a
plurality of fixed catalytic beds in cascade to
each other;

-- the gas feed stream contains methane, oxygen,

25   carbon dioxide and water in the following molar
proportions:
methane 1.0;
oxygen from 0.2 to 1.0;
carbon dioxide from 0 to 3.0;

30   water from 0 to 3.0; and

-- the process is carried out under adiabatic conditions;

by feeding the gas reactant stream upstream from the first catalytic bed and removing heat, by heat

5 exchange between the catalytic beds arranged in cascade, or

by feeding the gas reactant stream partially upstream from the first catalytic bed and partially, as a cold stream, between the catalytic beds arranged

10 in cascade, with said partial feeds being of same composition, or having different compositions from each other, with the proviso that methane is at least partially fed to the first catalytic bed and oxygen is subdivided between all of the catalytic beds.

15 The catalysts useful for the process according to the present invention are constituted by one or more metals from platinum group, selected from Rh, Ru, Ir, Pt and Pd, supported on a carrier selected from aluminum, magnesium, zirconium, silicon, cerium and/or

20 lanthanum oxides and/or spinels.

Said carrier can also be provided with surface-grafted silica moieties, and suitable processes for preparing such carriers with surface-grafted silica moieties are reported in the experimental examples

25 supplied in the following in the present application, in the above mentioned Italian patent applications and in United Kingdom patent application GB 2,240,284. Preferred carriers for such catalysts are alumina and/or magnesium oxide, possibily provided with

30 surface-grafted silica moieties.

The catalysts of the first catalytic bed contain rhodium in association with platinum or palladium, and the catalysts of the subsequent catalytic beds preferably contain two metals selected from rhodium,

5 ruthenium and iridium, with the overall percent contents of noble metals in the supported catalyst being comprised within the range of from 0.05 to 1.5% by weight, and preferably of from 0.1 to 1% by weight.

In order to be used as a stationary catalytic

10 bed, the catalysts will preferably be in granular form, with particle size comprised within the range of from 1 to 20 mm.

The catalytic beds used will be at least two, with their maximal number, dictated by practical

15 reasons, being of four or five. Preferably, the process will be carried out with either two or three catalytic beds in series to each other. These catalytic beds can be arranged inside a plurality of reactors arranged in series to each other, but

20 preferably, one single reactor containing a plurality of catalytic beds will be used.

According to the present invention, to the catalytic beds a gas stream is fed which contain methane and oxygen, and possibly also carbon dioxide

25 and/or water, preferably in the following molar proportions:

methane   1.0;

oxygen   0.4-0.6;

carbon dioxide 0-1.0; and

30 water   0-1.0.

As said hereinabove, the process is carried out under adiabatic conditions by feeding the gas reactant stream totally upstream from the first bed and removing heat, by heat exchange, from points between 5 the catalytic beds arranged in cascade.

According to a preferred embodiment, the process is carried out under adiabatic conditions by feeding the gas reactant stream partially upstream from the first catalytic bed and partially, as a cold stream, 10 between the catalytic beds arranged in cascade. The gas streams fed to the individual catalytic beds can have the same composition, or compositions different from one another. In the latter case, methane will be at least partially fed to the first catalytic bed and 15 the oxygen feed stream will suitably be subdivided between all catalytic beds.

In any case, by operating according to the present invention, synthesis gas is obtained by the effect of partial methane oxidation, and, possibly, 20 also owing to reforming phenomena, as a function of the fed reactants.

According to an embodiment of the present invention, to the first catalytic bed a gas stream is fed which contains methane, oxygen, carbon dioxide and 25 steam, and to the subsequent catalytic beds an oxygen stream is fed. Preferably, the process will be carried out with a molar ratio of methane, carbon dioxide and water fed to the first catalytic bed, of 1:0.5-1:0.3-1, and with a total oxygen amount of 0.4-0.6 mols per 30 each methane mol, fed as subdivided streams to each of

the several catalytic beds.

According to another embodiment, to the first catalytic bed a gas stream is fed which contains methane and oxygen, and to the subsequent catalytic
5   beds a mixture is fed which contains methane, oxygen and carbon dioxide. Preferably, the process will be carried out with a molar ratio of methane to oxygen fed to the catalytic beds of the order of 1:0.4, and with an amount of carbon dioxide of the order of 0.4
10 mols per each mol of methane.

According to a further embodiment, to the first catalytic bed, and to the subsequent ones, a gas stream is fed which contains methane, oxygen and carbon dioxide. The molar ratios of these reactants to
15 each other will preferably be of the order of 1:0.6:0.7-0.8.

According to a further embodiment, to the first catalytic bed a gas stream is fed which contains methane, oxygen and carbon dioxide, and to the
20 subsequent catalytic bed an oxygen stream will be fed. The process will preferably be carried out with a molar ratio of methane to carbon dioxide fed to the first catalytic bed of 1:0.3-0.6, and with a total oxygen amount of 0.5-0.6 mol per each mol of methane,
25 subdivided to the various catalytic beds.

It should be observed that according to the present disclosure, the term "oxygen" is understood to mean pure or substantially pure oxygen, or oxygen mixed with an inert gas, such as nitrogen, e.g., air.
30 In general, the process will be carried out with

inlet temperatures to the first bed of the order of 300-400°C and with outlet temperatures from said first bed, of the order of 700-870°C. The inlet temperatures to the beds downstream from the first bed will be of

5 the order of 450-730°C, and the outlet temperatures will be of the order of 770-850°C. The cooling between two adjacent beds will cause a decrease in temperature of from 10°C, up to as high values as 420°C and will normally be of the order of 120-170°C. The pressures

10 under which the process is carried out may generally be comprised within the range of from 0.1 to 10 MPa. The space velocities, under the reaction conditions, may generally be comprised within the range of from 1,000 to 50,000 h⁻¹ and will normally be of the order

15 of 5,000-20,000 h⁻¹.

By operating under these conditions, the mixture recovered at the outlet from the last catalytic bed, will contain hydrogen and carbon monoxide in a molar ratio to each other comprised within the range of from

20 about 0.9 to about 3 and normally of from about 1 to about 2.3.

It should be observed that in the case of exothermic reactions like the reaction of partial hydrocarbon oxidation [1], the expected reactant

25 conversion rates as calculated by means of equilibrium thermodynamic computations, vary as a function of temperature, according to the trend schematically shown in Figure 1 of the accompanying drawing tables. On the other hand it is known (O. Levenspiel,

30 "Chemical Reaction Engineering", John Wiley and Sons,

Inc., New York London) that the conversion rates, the reaction temperature and the reaction speed are mutually linked parameters. For exothermic reversible reaction (like the partial oxidation reaction [1])

5   which are catalyzed in a "Plug-Flow" reactor, a temperature increase kinetically favours the transformation of the reactants into the reaction products, but, opposite to this trend, the temperature increase decreases the maximal conversion rate which

10 can be obtained. In these cases, the optimal temperature variation can be obtained in reactors with a plurality of adiabatic layers with intermediate coolings induced by means of heat exchanges with heat recovery, or by means of the introduction of "cold"

15 gas streams of reactants between the layers. In Figure 1, "isospeed" curves are reported (i.e., curves along which the reaction speed remains constant with varying values of temperature and of reactants conversion), according to the typical trend of exothermic

20 processes. The peak points of isospeed lines determine pairs of values of temperature (T) and conversion (X_a). The line which connects all of these points with each other (i.e., the line which makes it possible the maximal reaction speed values to be obtained with

25 varying temperature) describes the optimal temperature progression for a Plug-Flow reactor in which an exothermic chemical process is being carried out. Similar considerations may be made in the case of endothermic processes. Such a curve can be

30 experimentally followed by means of a catalytic,

adiabatic-layer reactor provided with a plurality of reaction zones separated by temperature adjustment zones, as in the case of the process disclosed herein.

The following experimental examples are reported
5 in order to better illustrate the present invention.

Example_1

A laboratory reactor is used which is provided with two reaction zones, to which two different catalysts are charged.

10 The reactor was so accomplished as to make it possible the reactants (mixtures of methane, oxygen, steam and carbon dioxide) to be fed both to the reactor head, directly to the first catalytic bed (first adiabatic layer), and in the separation zone
15 between both catalytic beds (i.e., between the first and the second adiabatic layers).

The reactor is constituted by an alumina tube with an extremely low porosity and displaying high heat resistance and mechanical strength
20 characteristics. The alumina tube was fitted into a steel jacket. Around the steel tube, in the region of both reaction zones, two resistors are installed, the function of which is of compensating for the heat losses caused by the non-perfect adiabatic character
25 of the reactor (this is a drawback which is impossible to remove in such a type of testing in small-size laboratory reactors). Inside the alumina tube, there is fitted a thermocouple well. The steel sheath of the thermocouple well was coated with a thin gold layer in
30 order to prevent coal from being formed on its

surface. The temperatures inside both adiabatic layers were measured with the aid of two thermocouples which could be longitudinally moved along said beds.

The two catalysts used in these tests were prepared according to the following procedures.

Catalyst for the first reaction zone (first adiabatic layer).

Into a slurry constituted by a suspension of alpha-alumina in n-hexane, a solution of $Rh_4(CO)_{12}$ and $[Pd(C_5H_5O_2)_2]$ in the same solvent, was added dropwise. The solvent was then evaporated under vacuum and, after drying, the solid powder was pressed into pellets which, by crushing, yielded a granular solid with maximal particle diameter comprised within the range of from 2 to 2.5 mm. The catalyst volume charged to the first catalytic bed is of 5 cm^3, the Rh content in the catalyst is of 0.1% by weight, the palladium content is of 0.5% by weight.

Catalyst for the second reaction zone (second adiabatic layer).

In this case, a typical carrier for steam reforming catalysts was prepared, which contains magnesium oxides and alumina (Mg/Al = 7/1 mol/mol), and was obtained by means of a process comprising:

(i) co-precipitating aluminum and magnesium hydroxides, by increasing the pH value of an aqueous solution of $Mg(NO_3)_2$ and $Al(NO_3)_3 . 9H_2O$;

(ii) filtering the precipitate off and washing it;

(iii) drying and calcining the precipitate at 400°C,

(iv) "pelletizing" the solid powder;

(v) treating the pellets by further calcining them up to 1000°C and, after cooling, crushing the pellets in order to obtain a granular material with a maximal particle diameter of 2-2.5 mm.

5   The percent sodium level in the resulting carrier is lower than 0.1%. The carrier was then dispersed in a solution of n-hexane into which a solution, in the same solvent, of $Rh_4(CO)_{12}$ and $Ru_3(CO)_{12}$ had been added dropwise. After evaporation and vacuum drying, a

10   granular material was obtained which contained 0.1% by weight of Rh and 0.5% by weight of Ru. The catalyst volume charged to the second catalytic bed is of 5 cm^3.

Prior to the reaction, the catalysts were treated

15   at the temperature of 500°C, with H_2/N_2 streams containing increasing hydrogen levels. Then, to the inlet to the first catalytic bed a stream was fed which contained $CH_4:CO_2:O_2:H_2O$ in molar ratios of 1:1:0.5:0.3. The total flowrate of feedstock fed to

20   the first catalytic bed was of 50 Nl/hour, the gas stream inlet temperature was kept at 300°C, the inner reactor pressure was kept at 10 atm. Before entering the second adiabatic layer, the leaving stream from the first catalytic bed was mixed with a second stream

25   of oxygen pre-heated at 300°C, fed at a flowrate of 2.3 Nl/hour.

In Table 1, the main features of this experiment are reported.

TABLE 1

30   1st adiabatic layer

Catalyst:

-- composition: Rh (0,1%) + Pt (0,5%) on Al_2O_3

-- amount: 5 cc

Inlet composition:

5   -- CH_4:CO_2:O_2:H_2O = 1:1:0.5:0.3 (volume ratios)

Feed flowrate:

-- CH_4 = 17.90 Nl/hour

-- CO_2 = 17.90 Nl/hour

-- O_2 = 8.70 Nl/hour

10   -- H_2O = 5.30 Nl/hour

-- total = 50.00 Nl/hour

Temperatures:

-- inlet = 300°C

-- outlet = 745°C

15   IInd_adiabatic_layer

Catalyst:

-- composition: Rh (0.1%)+Ru (0.5%) on $MgAlO_x$

Inlet composition:

-- gas product from the Ist layer + added O_2

20   -- O_2 feed flowrate: 2.30 Nl/hour

Temperatures:

-- inlet = 730°C

-- outlet = 810°C

Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH_4	5.20	0.16
-- CO_2	23.46	0.73
-- H_2O	21.59	0.67
-- O_2	---	---
-- H_2	27.04	0.84

25

30

-- CO   22.68   0.71

    Molar ratio of H_2:CO at reactor outlet: 1.18:1.

Example_2

    The same experimental devices and the same catalysts as disclosed in experiment 1 were used, by feeding to the inlet to the first catalytic bed a reactant stream with a total flowrate of 50 Nl/hour and having the composition CH_4:CO_2:O_2:H_2O = 1:0.5:0.4:1 and feeding, upstream from the second catalytic bed, a stream of oxygen pre-heated at 300°C, with a flowrate of 3 Nl/hour.

    The main features of this second experiment are reported in Table 2.

TABLE_2

Ist_adiabatic_layer

Catalyst:

-- composition: Rh (0,1%) + Pt (0,5%) on Al_2O_3

-- amount: 5 cc

Inlet composition:

-- CH_4:CO_2:O_2:H_2O = 1:0.5:0.4:1 (volume ratios)

Feed flowrate:

-- CH_4 = 17.20 Nl/hour

-- CO_2 = 8.60 Nl/hour

-- O_2 = 7.00 Nl/hour

-- H_2O = 17.20 Nl/hour

-- total = 50.00 Nl/hour

Temperatures:

-- inlet = 300°C

-- outlet = 705°C

IInd_adiabatic_layer

Catalyst:

-- composition: Rh (0.1%) + Ru (0.5%) on MgAlO$_x$

-- amount: 3 cc

Inlet composition:

5 -- gas product from the Ist layer + added O$_2$

-- O$_2$ feed flowrate: 3.00 Nl/hour

Temperatures:

-- inlet = 690°C

-- outlet = 805°C

10 Composition at reactor outlet:

|	% by mol	Mols/hour
-- CH$_4$	5.10	0.16
-- CO$_2$	16.60	0.52
-- H$_2$O	29.27	0.92
-- O$_2$	---	---
-- H$_2$	34.11	1.07
-- CO	14.93	0.47

Molar ratio of H$_2$:CO at reactor outlet: 2.28:1.

Example 3

20   In this experiment, the same exerimental devices as disclosed in Examples 1 and 2 were used, but catalysts were used which contained noble metals deposited on alumina with surface-grafted silica moieties and magnesium carriers.

25 Catalyst for the first reaction zone (first adiabatic layer).

A commercial alumina sypplied by AKZO, having a surface area of approximately of 200 m^2/g was suspended, with stirring, in a tetraethyl silicate

30 (TES) solution. The temperature was kept comprised

within the range of from 80 to 90°C. Under these conditions, a trans-esterification reaction took place which is represented by equation [8] and led to the development of ethanol in gas form:

5    $Si(OC_2H_5)_4 + Al-OH \longrightarrow Al-O-Si(OC_2H_5)_3 + C_2H_5-OH$
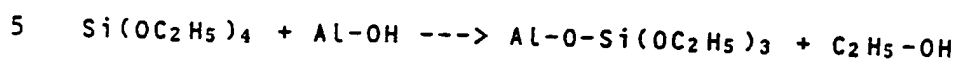
A gas stream of anhydrous nitrogen was fed to the reaction environment. Gas-chromatographic analyses on the leaving gas showed that ethanol had been formed. The reaction was regarded as concluded when in the gas

10   stream the presence of ethanol was no longer detectable. At this point, the temperature was increased up to 180°C, in order to distil off any unreacted TES. The unreacted ethoxy groups bonded to silicon atoms which, in their turn, were anchored to

15   the surface, were then hydrolized by feeding, at 200°C, a nitrogen stream saturated with steam. The so obtained solid material was heated up to 800°C and was kept at this temperature during 10 hours. After cooling, the material was used as a carrier, onto

20   which rhodium and platinum were deposited. The finished catalyst contained 0.1% of rhodium and 0.5% by weight of platinum.

Catalyst_for_the_second_reaction_zone_(second_adiabatic_layer).

25   The surface silica-grafting process as disclosed above was repeated on a carrier of commercial magnesium oxide having a surface area of 150 m²/g. Onto this magnesium oxide with surface-grafted silica moieties obtained by means of this procedure, 0.1% by

30   weight of Rh and 0.5% by weight of Ru were then

deposited according to the same procedure as disclosed in Example 1.

The catalytic test was carried out according to the same procedure as disclosed in Examples 1 and 2. After a reducing treatment, a stream containing $CH_4:CO_2:O_2:H_2O$ in molar ratios of 1.0:1.0:0.4:1.0 was fed to the inlet to the first catalytic bed. Before entering the second catalytic bed, the stream leaving from the first catlytic bed was admixed with an oxygen stream fed at a flowrate of 1.8 Nl/hour.

The main features of this experiment are disclosed in Table 3.

TABLE 3

Ist adiabatic layer

Catalyst:

-- composition: Rh (0,1%) + Pt (0,5%) on silica-grafted alumina

-- amount: 5 cc

Inlet composition:

-- $CH_4:CO_2:O_2:H_2O$ = 1.0:1.0:0.4:1.0 (volume ratios)

Feed flowrate:

-- CH_4 = 14.70 Nl/hour

-- CO_2 = 14.70 Nl/hour

-- O_2 = 5.90 Nl/hour

-- H_2O = 14.70 Nl/hour

-- total = 50.00 Nl/hour

Temperatures:

-- inlet = 300°C

-- outlet = 698°C

IInd adiabatic layer

Catalyst:

-- composition: Rh (0.1%) + Ru (0.5%) on silica-
grafted magnesium oxide

-- amount: 3 cc

5 Inlet composition:

-- gas product from the Ist layer + added O_2

-- O_2 feed flowrate: 1.47 Nl/hour

Temperatures:

-- inlet = 685°C

10 -- outlet = 790°C

Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH_4	4.41	0.13
-- CO_2	21.11	0.64
-- H_2O	26.83	0.81
-- O_2	---	---
-- H_2	29.65	0.90
-- CO	18.01	0.55

Molar ratio of H_2:CO at reactor outlet: 1.64:1.

20   Example_4

In this experiment, to the first catalytic bed, a
volume of 5 cm³ was charged of a catalyst containing
0.1% by weight of Rh and 0.5% by weight of Pd. The
metals were deposited according to the same procedure
25 as disclosed in Example 1, on a carrier constituted by
magnesium and aluminum oxides (Mg:Al = 7:1 mol/mol),
using a solution containing $Rh_4(CO)_{12}$ and
$[Pd(C_5H_5O_2)_2]$ in a hydrocarbon solvent.

To the second catalytic bed, a volume of 4 cm³
30 was then charged of a catalyst containing 0.5% by

weight of Ru and 0.5% by weight of Ir, deposited on magnesium and aluminum mixed oxide. The deposition of these metals onto the carrier was accomplished by adding, dropwise, a solution of $Ir_4(CO)_{12}$ and

5    $Ru_3(CO)_{12}$ in a hydrocarbon solvent, to a suspension of the carrier in the same solvent, as disclosed in Example 1.

After a treatment in a H_2-N_2 stream at 500°C, a stream of CH_4 and O_2 ($CH_4:O_2$ = 60:25 by vol/vol) was

10   added to the first catalytic bed, and upstream from the second catalytic bed, a stream of CH_4, O_2 and CO_2 ($CH_4:O_2:CO_2$ = 40:25:40 by vol/vol) was admixed to the gas stream from the first catalytic bed.

The main features obtained during the catalytic

15   test are reported in Table 4.

TABLE 4

Ist_adiabatic_layer

Catalyst:

-- composition: Rh (0,1%) + Pt (0,5%) on $MgAlO_x$

20   -- amount: 5 cc

Inlet composition:

-- $CH_4:O_2$ = 60:25 (volume ratios)

Feed flowrate:

-- CH_4 = 15.78 Nl/hour

25   -- O_2 = 6.60 Nl/hour

-- total = 22.38 Nl/hour

Temperatures:

-- inlet = 300°C

-- outlet = 745°C

30   IInd_adiabatic_layer

Catalyst:

-- composition: Ir (0.5%) + Ru (0.5%) on $MgAlO_x$

-- amount: 4 cc

Inlet composition:

5   -- gas product from the Ist layer + CH_4 + O_2 + CO_2 added

-- feed flowrate:

-- CH_4 = 10.52 Nl/hour

-- O_2 = 6.50 Nl/hour

10   -- CO_2 = 10.50 Nl/hour

-- total = 27.52 Nl/hour

Temperatures:

-- inlet = 581°C

-- outlet = 815°C

15   Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH_4	13.95	0.43
-- CO_2	14.47	0.45
-- H_2O	14.90	0.46
20 -- O_2	---	---
-- H_2	32.40	1.01
-- CO	24.28	0.76

Molar ratio of H_2:CO at reactor outlet: 1.33:1.

Example_5

25   In this case, the process of catalytic partial oxidation in an adiabatic reactor with layer configuration was studied by using three Plug-Flow reactors (which are referred to in the following as "R1", "R2", "R3"), each containing one catalytic bed.

30   The characteristics of said three reactors are

analagous to those as of the reactor disclosed in Figure 4. A mixture of CH_4, O_2, CO_2, fed with a total gas flowrate of 149 Nl/hour ($CH_4:O_2:CO_2$ = 1:0.6:0.8 by vol/vol) was subdivided into three streams. The first

5 stream (flowrate 60.1 Nl/h) was fed to the inlet to reactor R1; the second stream (flowrate 53.3 Nl/h) was fed to a point between reactor R1 and reactor R2; the third stream (flowrate 35.6 Nl/h) was fed to a point between reactor R2 and reactor R3.

10 The temperature of the stream fed to the inlet to the first reactor was kept at 300°C, and the inlet temperatures to the second and third reactors were kept at 450°C. The catalyst contained in reactor R1 (catalyst volume: 3 cm^3) was composed by Rh (0.1% by

15 weight) and Pd (0.5% by weight) deposited on a support constituted by a mixed magnesium and aluminum oxide, prepared by operating according to the same procedure as disclosed in Example 1.

The catalyst contained in reactor R2 (catalyst

20 volume: 4 cm^3) was composed by Rh (0.1% by weight) and Ir (0.5% by weight), deposited on the same carrier of magnesium and aluminum oxides. The catalyst was prepared according to the same procedure as disclosed in Examples 1 and 3. The catalyst contained in R3 was

25 composed by Rh (0.1% by weight) and Ru (0.5% by weight), deposited, also in this case, onto the same magnesium and aluminum oxide. The catalyst was prepared according to the same procedures as disclosed in Example 1.

30 In Table 5, the main features and the results of

the present experiment are reported.

TABLE 5

Ist adiabatic layer

Catalyst:

5   -- composition: Rh (0,1%) + Pt (0,5%) on MgAlO$_x$

-- amount: 3 cc

Inlet composition:

-- CH$_4$:O$_2$:CO$_2$ = 100:60:80 (volume ratios)

Feed flowrate:

10   -- CH$_4$ = 25.10 Nl/hour

-- CO$_2$ = 20.00 Nl/hour

-- O$_2$ = 15.00 Nl/hour

-- total = 60.10 Nl/hour

Temperatures:

15   -- inlet = 300°C

-- outlet = 865°C

IInd adiabatic layer

Catalyst:

-- composition: Rh (0.1%)+Ir (0.5%) on MgAlO$_x$

20   -- amount: 4 cc

Inlet composition:

-- gas product from the Ist layer + CH$_4$ + O$_2$ + CO$_2$
added

-- feed flowrate:

25   -- CH$_4$ = 22.6 Nl/hour

-- O$_2$ = 17.5 Nl/hour

-- CO$_2$ = 13.2 Nl/hour

-- total   = 53.3 Nl/hour

Temperatures:

30   -- inlet = 450°C

-- outlet = 825°C

IIIrd_adiabatic_layer

Catalyst:

-- composition: Rh (0.1%) + Ru (0.5%) on MgAlO$_x$

5   -- amount: 5 cc

Inlet composition:

-- gas product from the IInd layer + CH$_4$ + O$_2$ + CO$_2$
   added

-- feed flowrate:

10   -- CH$_4$ = 15.0 Nl/hour

-- O$_2$ = 11.9 Nl/hour

-- CO$_2$ = 8.7 Nl/hour

-- total   = 35.6 Nl/hour

Temperatures:

15   -- inlet = 450°C

-- outlet = 785°C

Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH$_4$	5.74	0.54
-- CO$_2$	18.23	1.82
-- H$_2$O	16.89	1.59
-- O$_2$	---	---
-- H$_2$	30.33	2.87
-- CO	28.84	2.72

25   Molar ratio of H$_2$:CO at reactor outlet: 1.055:1.

Examples_6-8

The same experimental apparatus and the same
catalysts as disclosed in Example 5 were used in
Examples 6, 7 and 8 in order to obtain a catalytic
30   partial oxidation process on a three-layer catalyst,

to which a feedstock consisting of methane, CO_2 and oxygen was fed. In these cases, differently from the experiment as disclosed in Example 5, the whole amounts of CH_4 and CO_2 were fed to the inlet to the

5   first reactor R1, and the oxygen feed was subdivided into three streams which were fed to the inlet of R1, to an intermediate point between R1 and R2, and to an intermediate point between R2 and R3. Examples 6, 7 and 8 are different from each other owing to the inlet

10 temperatures of the gas streams to the three adiabatic layers. Different inlet temperatures to the adiabatic layers have determined different temperatures and composition of the bed leaving streams.

In following Tables 6, 7 and 8, the main features

15 and the results obtained in Examples 6, 7 and 8 are reported.

TABLE 6

1st adiabatic layer

Catalyst:

20 -- composition: Rh (0,1%) + Pt (0,5%) on MgAlO$_x$

-- amount: 4 cc

Inlet composition:

-- CH_4:O_2:CO_2 = 100:30:60 (volume ratios)

Feed flowrate:

25 -- CH_4 = 68.30 Nl/hour

-- CO_2 = 41.00 Nl/hour

-- O_2 = 20.50 Nl/hour

-- total = 129.80 Nl/hour

Temperatures:

30 -- inlet = 300°C

-- outlet = 710°C

IInd_adiabatic_layer

Catalyst:

-- composition: Rh (0.1%) + Ir (0.5%) on MgAlO$_x$

5   -- amount: 4 cc

Inlet composition:

-- gas product from the Ist layer + O$_2$ added

-- feed flowrate:

-- O$_2$ = 13.6 Nl/hour

10   -- total   = 13.6 Nl/hour

Temperatures:

-- inlet = 450°C

-- outlet = 775°C

IIIrd_adiabatic_layer

15   Catalyst:

-- composition: Rh (0.1%) + Ru (0.5%) on MgAlO$_x$

-- amount: 5 cc

Inlet composition:

-- gas product from the IInd layer + O$_2$ added

20   -- feed flowrate:

-- O$_2$ = 6.8 Nl/hour

-- total   = 6.8 Nl/hour

Temperatures:

-- inlet = 450°C

25   -- outlet = 778°C

Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH$_4$	7.2	0.69
-- CO$_2$	16.1	1.54
-- H$_2$O	16.6	1.59

30

```
-- O₂              ---           ---
-- H₂             32.6          3.12
-- CO             27.6          2.64
```

Molar ratio of H$_2$:CO at reactor outlet: 1.1818:1.

TABLE 7

Ist adiabatic layer

Catalyst:

-- composition: Rh (0,1%) + Pt (0,5%) on MgAlO$_x$

-- amount: 4 cc

Inlet composition:

-- CH$_4$:O$_2$:CO$_2$ = 100:30:60 (volume ratios)

Feed flowrate:

-- CH$_4$ = 68.30 Nl/hour

-- CO$_2$ = 41.00 Nl/hour

-- O$_2$ = 20.50 Nl/hour

-- total = 129.80 Nl/hour

Temperatures:

-- inlet = 300°C

-- outlet = 715°C

IInd adiabatic layer

Catalyst:

-- composition: Rh (0.1%) + Ir (0.5%) on MgAlO$_x$

-- amount: 4 cc

Inlet composition:

-- gas product from the Ist layer + O$_2$ added

-- feed flowrate:

-- O$_2$ = 13.6 Nl/hour

-- total   = 13.6 Nl/hour

Temperatures:

-- inlet = 550°C

-- outlet = 797°C

IIIrd_adiabatic_layer

Catalyst:

-- composition: Rh (0.1%) + Ru (0.5%) on MgAlO$_x$

-- amount: 5 cc

Inlet composition:

-- gas product from the IInd layer + O$_2$ added

-- feed flowrate:

-- O$_2$ = 6.8 Nl/hour

-- total   = 6.8 Nl/hour

Temperatures:

-- inlet = 550°C

-- outlet = 816°C

Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH$_4$	4.6	0.46
-- CO$_2$	16.1	1.34
-- H$_2$O	15.6	1.56
-- O$_2$	---	---
-- H$_2$	35.9	3.60
-- CO	30.6	3.07

Molar ratio of H$_2$:CO at reactor outlet: 1.172:1.

TABLE_8

Ist_adiabatic_layer

Catalyst:

-- composition: Rh (0,1%) + Pt (0,5%) on MgAlO$_x$

-- amount: 4 cc

Inlet composition:

-- CH$_4$:O$_2$:CO$_2$ = 100:30:60 (volume ratios)

Feed flowrate:

-- CH$_4$ = 68.30 Nl/hour

-- CO$_2$ = 41.00 Nl/hour

-- O$_2$ = 20.50 Nl/hour

-- total = 129.80 Nl/hour·

5 Temperatures:

-- inlet = 400°C

-- outlet = 722°C

IInd_adiabatic_layer

Catalyst:

10 -- composition: Rh (0.1%) + Ir (0.5%) on MgAlO$_x$

-- amount: 4 cc

Inlet composition:

-- gas product from the Ist layer O$_2$ added

-- feed flowrate:

15 -- O$_2$.   = 13.6 Nl/hour

-- total   = 13.6 Nl/hour

Temperatures:

-- inlet = 600°C

-- outlet = 812°C

20 IIIrd_adiabatic_layer

Catalyst:

-- composition: Rh (0.1%) + Ru (0.5%) on MgAlO$_x$

-- amount: 5 cc

Inlet composition:

25 -- gas product from the IInd layer + O$_2$ added

-- feed flowrate:

-- O$_2$ = 6.8 Nl/hour

-- total   = 6.8 Nl/hour

Temperatures:

30 -- inlet = 600°C

-- outlet = 841°C

Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH_4	3.3	0.34
-- CO_2	11.9	1.22
-- H_2O	15.1	1.55
-- O_2	---	---
-- H_2	37.6	3.87
-- CO	32.2	3.31

Molar ratio of $H_2:CO$ at reactor outlet: 1.169:1.

Example 9

The same experimental apparatus as disclosed in Examples 5-8 was used in order to study the reactions of catalytic partial oxidation of mixtures of $CH_4:O_2:CO_2$ = 100:60:30 (by vol/vol). In this case, the content of CO_2 was kept at lower values than as in the preceding examples. Also in this case, the oxygen stream was subdivided into partial streams which were fed both to the inlet to R1, and to an intermediate point between R1 and R2, as well as to an intermediate point between R2 and R3. Furthermore (by pre-heating the gas reactant streams), inlet temperatures to the catalytic beds were tested which were higher than in the preceding examples. The catalyst used in reactor R1 (Ist adiabatic layer) contained Rh (0.1% by weight) and Pt (0.5% by weight) deposited on a mixed aluminum and magnesium oxide. The preparation procedures used have already been disclosed in the preceding examples.

The catalysts contained in the second reactor (R2) and in the third reactor (R3) (i.e., the second

and third adiabatic layers) were the same as used in Examples 5-8 and contained Rh and, respectively, Ir, deposited on an aluminum and magnesium oxide, and Rh and Ru deposited on the same support.

5   In following Table 9, the main features of the experiment are reported.

TABLE 9

Ist adiabatic layer

Catalyst:

10   -- composition: Rh (0,1%) + Pt (0,5%) on MgAlO$_x$

-- amount: 4 cc

Inlet composition:

-- CH$_4$:O$_2$:CO$_2$ = 100:30:30 (volume ratios)

Feed flowrate:

15   -- CH$_4$ = 79.00 Nl/hour

-- CO$_2$ = 23.70 Nl/hour

-- O$_2$ = 23.70 Nl/hour

-- total = 126.40 Nl/hour

Temperatures:

20   -- inlet = 400°C

-- outlet = 761°C

IInd adiabatic layer

Catalyst:

-- composition: Rh (0.1%) + Ir (0.5%) on MgAlO$_x$

25   -- amount: 4 cc

Inlet composition:

-- gas product from the Ist layer O$_2$ added

-- feed flowrate:

-- O$_2$ = 15.8 Nl/hour

30   -- total   = 15.8 Nl/hour

Temperatures:

-- inlet = 600°C

-- outlet = 853°C

IIIrd_adiabatic_layer

5   Catalyst:

-- composition: Rh (0.1%) + Ru (0.5%) on MgAlO$_x$

-- amount: 5 cc

Inlet composition:

-- gas product from the IInd layer + O$_2$ added

10   -- feed flowrate:

-- O$_2$ = 7.9 Nl/hour

-- total   = 7.9 Nl/hour

Temperatures:

-- inlet = 600°C

15   -- outlet = 841°C

Composition_at_reactor_outlet:

	% by mol	Mols/hour
-- CH$_4$	3.1	0.34
-- CO$_2$	6.9	0.76
-- H$_2$O	12.3	1.34
-- O$_2$	---	---
-- H$_2$	45.9	5.03
-- CO	31.8	3.48

Molar ratio of H$_2$:CO at reactor outlet: 1.445:1.

25

30

CLAIMS

1.   A catalytic process for preparing a synthesis gas from methane, oxygen, and, optionally, carbon dioxide and/or water, wherein:

5   the catalyst used is a noble metal catalyst supported on a solid carrier, arranged as a plurality of fixed catalytic beds in cascade to each other; the gas feed stream comprises methane, oxygen, and, optionally, carbon dioxide and/or water in the

10   following molar proportions:

methane 1.0;

oxygen from 0.2 to 1.0;

carbon dioxide from 0 to 3.0;

water 0 to 3.0; and

15   the process is carried out under adiabatic conditions either:

(a) by feeding the gas reactant stream upstream from the first catalytic bed and removing heat by heat exchange between the catalytic beds arranged

20   in cascade, or

(b) by feeding the gas reactant stream partially upstream from the first catalytic bed and partially between the catalytic beds arranged in cascade, with said partial feeds being of the same or different

25   compositions, with the proviso that methane is at least partially fed to the first catalytic bed and oxygen is subdivided between all of the catalytic beds.

2.   A process according to claim 1, wherein the gas feed stream contains the reactants in the following

30   molar proportions:

methane 1.0;

oxygen from 0.4 to 0.6;

carbon dioxide from 0 to 1.0; and

water from 0 to 1.0.

35   3.   A process according to claim 1 or 2, wherein the catalyst comprises one or more platinum group

metals selected from Rh, Ru, Ir, Pt and Pd, supported on a carrier selected from aluminum, magnesium, zirconium, silicon, cerium and/or lanthanum oxides and/or spinels, or from silica-treated products of such
5 carriers.

4. A process according to claim 3, wherein the catalyst of the first catalytic bed comprises rhodium in association with platinum or palladium, and the catalyst(s) of the subsequent catalytic bed contain two
10 metals selected from rhodium, ruthenium and iridium, with the overall content of nobel metals in the supported catalyst being from 0.05 to 1.5% by weight, preferably from 0.1 to 1% by weight.

5. A process according to any of claims 1 to 4,
15 wherein the catalysts are in granular form with a particle size of from 1 to 20 mm, and are arranged in at least two and up to five catalytic beds, preferably either two or three catalytic beds.

6. A process according to any of claims 1 to 5,
20 wherein, to the first catalytic bed, there is fed a gas steam which comprises methane, oxygen, carbon dioxide and stream, and to the subsequent catalytic bed there is fed a stream comprising oxygen.

7. A process according to claim 6, wherein the
25 process is carried out with a molar ratio of methane, carbon dioxide and water fed to the first catalytic bed of 1:0.5-1:0.3-1, and with a total amount of oxygen of 0.4-0.6 mol per mol of methane, subdivided between the catalytic beds.

30 8. A process according to any of claims 1 to 5, wherein, to the first catalytic bed, there is fed a gas stream which comprises methane and oxygen, and, to the subsequent catalytic bed(s), there is fed a mixture which comprises methane, oxygen and carbon dioxide.

35 9. A process according to claim 8, wherein the process is carried out with a molar ratio of methane to

oxygen fed to the catalytic beds of the order of 1:0.4, and with an amount of carbon dioxide of the order of 0.4 mol per mol of methane.

10. A process according to any of claims 1 to 5, wherein, to the first catalytic bed and to the subsequent bed(s), there is fed a gas stream which comprises methane, oxygen and carbon dioxide.

11. A process according to claim 10, wherein the process is carried out with molar ratios of said reactants of the order of 1:0.6:0.7-0.8.

12. A process according to any of claims 1 to 5, wherein, to the first catalytic bed, there is fed a gas stream which comprises methane, oxygen and carbon dioxide, and, to the subsequent catalytic bed(s), there is fed a stream comprising oxygen.

13. A process according to claim 12, wherein the process is carried out with a molar ratio of methane to carbon dioxide fed to the first catalytic bed of 1:0.3-0.6, and with a total amount of oxygen of 0.5-0.6 mol per mol of methane, subdivided between the catalytic beds.

14. A process according to any of claims 1 to 13, wherein the process is carried out with an inlet temperature to the first bed of the order of 300-400°C and with outlet temperatures from said first bed of the order of 700-870°C, with an inlet temperature, to the bed(s) downstream from the first bed, of the order of 450-730°C and outlet temperatures of the order of 770-850°C, with the cooling between two adjacent beds causing a temperature decrease of from at least 10°C up to 420°C, and preferably of the order of 120-170°C.

15. A process according to any of claims 1 to 14, wherein the process is carried out under a pressure of from 0.1 to 10 MPa and with a space velocity value, under the reaction conditions, of from 1,000 to 50,000 h^{-1}.

16. A process according to claim 1, substantially as described in any of the Examples.

17. Synthesis gas prepared by a process according to any of claims 1 to 16.

Rei...ant Technical Fields	Search Examiner J F JENKINS
(i) UK Cl (Ed.M) C5E (EAR, EAS)	
(ii) Int Cl (Ed.5) C01B 3/34, 3/36, 3/38, 3/40	Date of completion of Search 11 APRIL 1994
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASE : WPI	Documents considered relevant following a search in respect of Claims :- 1 TO 17

Categories of documents

X:	Document indicating lack of novelty or of inventive step.	P:	Document published on or after the declared priority date but before the filing date of the present application.
Y:	Document indicating lack of inventive step if combined with one or more other documents of the same category.	E:	Patent document published on or after, but with priority date earlier than, the filing date of the present application.
A:	Document indicating technological background and/or state of the art.	&:	Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
P,A	EP 0576096 A2	(SHELL INT) - see page 3 lines 31-43	
Y	EP 0548679 A1	(IDEMITSU KOSAN) - see page 2 lines 44-52	1
Y	EP 0330751 A2	(UHDE GMBH) - see Figure	1, 6, 7
A	EP 0303438 A2	(DAVY McKEE) - see Figure 1, Example and column 7 lines 10-15	
Y	WO 93/01130 A1	(UNIVERSITY OF WARWICK) - see Claim 2	1
Y	US 4897253	(J JENKINS) - see column 2 lines 23-39	1
Y	US 4844837	(R M HECK) - see column 5 lines 17-30	1
A	US 4620940	(D V QUANG) - see Claim 1	